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Global N removal by freshwater aquatic systems using a spatially distributed, within-basin approach

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Global N removal by freshwater aquatic systems using a spatially distributed, within-basin approach

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[1] We explored the role of aquatic systems in the global N cycle using a spatially distributed, within-basin, aquatic nitrogen (N) removal model, implemented within the Framework for Aquatic Modeling in the Earth System (FrAMES-N). The model predicts mean annual total N (TN) removal by small rivers (with drainage areas from 2.6–1000 km^2), large rivers, lakes, and reservoirs, using a 30′ latitude × longitude river network to route and process material from continental source areas to the coastal zone. Mean annual aquatic TN removal (for the mid-1990s time period) is determined by the distributions of aquatic TN inputs, mean annual hydrological characteristics, and biological activity. Model-predicted TN concentrations at basin mouths corresponded well with observations (median relative error = −12%, interquartile range of relative error = 85%), an improvement over assumptions of uniform aquatic removal across basins. Removal by aquatic systems globally accounted for 14% of total N inputs to continental surfaces, but represented 53% of inputs to aquatic systems. Integrated aquatic removal was similar in small rivers (16.5% of inputs), large rivers (13.6%), and lakes (15.2%), while large reservoirs were less important (5.2%). Bias related to runoff suggests improvements are needed in nonpoint N input estimates and/or aquatic biological activity. The within-basin approach represented by FrAMES-N will improve understanding of the freshwater nutrient flux response to anthropogenic change at global scales.

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1. Introduction

[2] Riverine flux of nitrogen (N) from continents to coastal oceans has increased considerably because of human activities [*Green et al.*, 2004; *Seitzinger et al.*, 2005], leading to eutrophication, toxic algal blooms, anoxic dead zones in coastal areas [*Anderson et al.*, 2002; *Rabalais et al.*, 2002; *Smith et al.*, 1999], and degraded drinking water supplies [*Townsend et al.*, 2003]. Although environmental impacts linked to increased N exports are considerable, only a small proportion of N loaded onto the landscape reaches the coastal zone [*Boyer et al.*, 2002; *Howarth et al.*, 1996]. Recent regression models of whole watershed export developed at regional to global scales suggest that the proportion of N inputs retained or denitrified (henceforth referred to as removal) is related to basin characteristics, including precipitation, runoff, water residence time, and temperature [*Dumont et al.*, 2005; *Green et al.*, 2004; *Howarth et al.*, 2006]. While the whole basin regression approach can suggest the presence of controls, mechanistic models that simulate the geospatial relationships between loading and sequestration/loss are needed to better explain the mechanisms responsible for the observed removal rates and to predict responses to global change.

[3] Explaining the global fate of N requires approaches that incorporate spatially varying (1) local N input rates, (2) hydrological forcings, and (3) biological activity in both terrestrial and aquatic systems. Spatially distributed models

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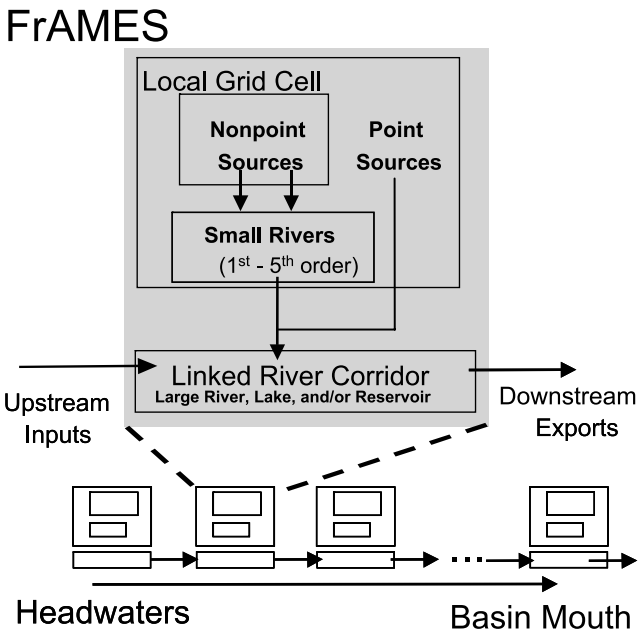

Figure 1. Elements of the Framework for Aquatic Modeling in the Earth System (FrAMES-N).

have been developed for individual basins [*Donner et al.*, 2002], and are beginning to be developed at the global scale [*Bouwman et al.*, 2005; *Seitzinger et al.*, 2006; *van Drecht et al.*, 2003]. Several recent studies have quantified N inputs onto global land surfaces (compared by *van Drecht et al.* [2005]), one of which was applied as input to a spatially distributed, terrestrial N ecosystem model [*Bouwman et al.*, 2005]. Using a priori parameterization of terrestrial processes, this model yielded good predictions of total N (TN) export from large basins. However, exports were generally over predicted with considerable unexplained variability. In their model, surface waters were assigned a globally constant removal proportion once material left the terrestrial system. This approach disregards the spatial variability of aquatic removal within and across basins.

[4] N removal in aquatic systems is a function of the spatial distribution of N inputs to inland waterways, river network geomorphology, hydrological conditions, and intensity of biological activity [*Wollheim et al.*, 2006]. River network models have integrated these factors to explore the magnitude and variability of aquatic N removal in individual basins [*Alexander et al.*, 2000; *Donner et al.*, 2002], or across regional basins with similar climate conditions [*Seitzinger et al.*, 2002]. Such models have not been applied at the global scale to explore how variability in runoff, lake distribution, basin size, and temperature might influence aquatic N removal capacity across basins, and the resulting impact on the global N budget. Application of such a model requires that various water body types be integrated at the global scale in a river network context.

[5] Here we apply an aquatic N removal model within the Framework for Aquatic Modeling in the Earth System (FrAMES-N) to explore the role of freshwater systems in the global N cycle at mean annual timescales. This spatially distributed aquatic model complements the terrestrial global N model of *Bouwman et al.* [2005] applied to the mid-1990s time frame. Our goals are to (1) determine whether a spatially explicit aquatic model linked with a global terrestrial model improves N export predictions at basin mouths, (2) quantify the role of aquatic systems in determining the fate of N at the global scale in a spatially explicit manner, and (3) evaluate the major controls of aquatic removal.

2. Methods

[6] The topological structure of the Framework for Aquatic Modeling in the Earth System (FrAMES-N) is based on the 30-min global river network (STN-30; *Vörösmarty et al.* [2000]) modified to integrate small rivers, lakes, and reservoirs (Figure 1). Mean annual TN removal in the water bodies within each grid cell is modeled as a function of upstream plus local nutrient inputs, hydrological characteristics, and biological activity.

2.1. Removal Model

[7] TN flux exported from each grid cell i (kg a^{-1}) is based on a modification of the model of *Green et al.* [2004] and determined as

$$TN_i = \left(LocalPoint_i + \left(LocalNonPoint_i * TE_{localriver_i}\right) + UpstreamIn_i\right) * TE_{largeriver_i} * TE_{lake_i} * TE_{reservoir_i} \quad (1)$$

where LocalPoint = all point sources in grid cell i (kg a^{-1}), LocalNonPoint = all nonpoint N inputs to the aquatic system in i (kg a^{-1}), UpstreamIn = TN inputs from all grid cells immediately upstream from i (kg a^{-1}), TE = transfer efficiency (TE = 1 − R, where R is the proportion of inputs removed by the water body; unitless) associated with the local river network, large river channels, lakes, and/or reservoirs within the grid cell.

[8] TE for each water body is a function of hydrologic conditions and biological activity. For N over annual timescales, benthic processes are assumed to dominate N removal via denitrification or sequestration, and can be generically represented as

$$TE = \exp\left(\frac{-\upsilon_f}{H_L}\right) \quad (2)$$

where υ_f represents biological activity in the form of the uptake velocity, or mass transfer coefficient of the nutrient (m a^{-1}) and H_L represents hydrological conditions in the form of the hydraulic load (m a^{-1}).

[9] Under the assumption that benthic processes dominate, (2) clearly separates biological and hydrological factors and can be used to scale biological activity across water bodies of widely varying size [*Wollheim et al.*, 2006]. υ_f is discussed further in section 2.4. H_L can be calculated in several related ways:

$$H_L = \frac{dv}{L} = \frac{d}{\tau} = \frac{Q}{A_{sw}} = \frac{Q}{wL} \quad (3)$$

where d is mean water depth (m), v is mean water velocity (m a^{-1}), w is mean channel width (m), L is channel

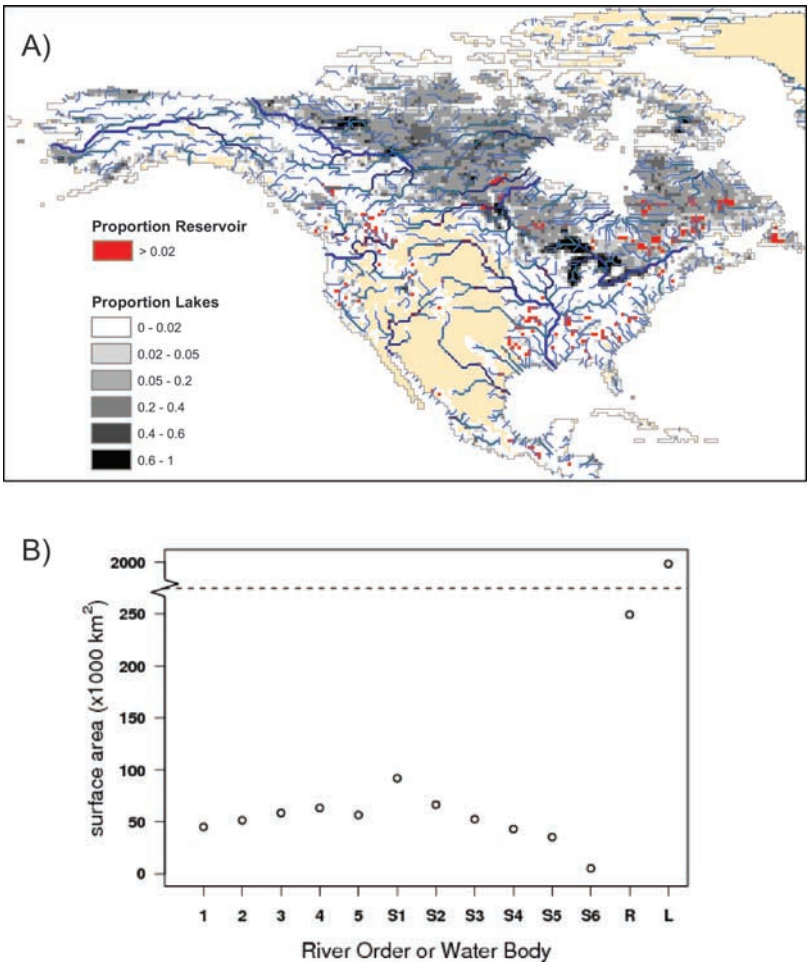

Figure 2. (a) North American portion of the STN-30 river network integrating the distribution of large rivers (sixth order and higher, with eighth order and higher shown), lakes, and large reservoirs as a proportion of grid cell area. Regions without runoff are shown in beige. A network of small rivers occurs within each flowing grid cell, and is implicitly represented as described in section 2.2. (b) Sum of global benthic surface area for low-order rivers (1–5), high-order rivers (S1–S6, equivalent to sixth–eleventh order), reservoirs (*R*), and lakes (*L*). The surface areas of rivers are derived from the lengths, number, and widths in Figure S1. Note break in *y* axis scale.

length (m), τ is residence time (a^{-1}), Q is discharge ($m^3\ a^{-1}$), and A_{sw} is surface area of the water body (m^2).

[10] $TE_{localriver}$ is determined using (2) and the geomorphic model described by *Wollheim et al.* [2006] in which removal by each stream order within the local river network is determined and integrated to calculate total subgrid network removal. $TE_{largeriver}$, TE_{lake}, and $TE_{reservoir}$ are determined using (2) on the basis of discharge through each grid cell and benthic surface area of each class of water body within the cell.

2.2. River Network Representation

[11] All water bodies are georeferenced to the STN-30 river network, where each grid cell represents 1000–3000 km^2 of land surface depending on latitude [*Vörösmarty et al.*, 2000]. STN-30 defines the flow path of material through large rivers to the coastal zone (Figure 2a). Length of large river flowing through each grid cell is defined by grid cell size, direction of flow, and a sinuosity factor of 1.3 [*Fekete et al.*, 2001].

[12] In addition to the large river represented explicitly by the STN-30, each grid cell contains at least one fifth- to sixth-order river network at the 1:62,500 scale [*Vörösmarty et al.*, 2000]. We define the characteristics of the subgrid river network for the nonlake portion of each cell using accepted geomorphic principles [*Leopold et al.*, 1964]. The number, mean drainage area, and stream length are calculated for each subgrid order on the basis of specified first-order drainage area and length, and drainage area (R_A), length (R_L), and bifurcation (R_B) ratios [*Dingman*, 1994]. Geomorphic parameters are assumed to be globally uniform, consistent with both STN-30 characteristics (Table 1) [*Vörösmarty et al.*, 2000] and observations [*Leopold et al.*, 1964].

Table 1. Parameters Used in the Base Scenario

Parameter	Symbol	Value	Source
Hydrological			
Drainage Area Ratio	R_A	4.7	[a]
Stream Number Ratio	R_B	4.5	[a]
Mean Length Ratio	R_L	2.3	[a]
Drainage area: first-order stream	A_1, km^2	2.6	[a]
Mean length: first-order stream	L_1, km	1.6	[a]
STN-30 sinuosity	S	1.3	[b]
Width constant	*a*, m	8.3	[a,c]
Width exponent	*b*	0.52	[a,c]
Biological			
Vertical velocity of N at T_{ref}	υ_{fref}, m a^{-1}	35	[d,e]
Temperature adjustment	Q_{10}	2	[f]
Reference temperature	T_{ref}, °C	20	[g]

[a] *Leopold et al.* [1964].
[b] *Fekete et al.* [2001].
[c] David Bjerklie, USGS, personal communication, 2006.
[d] *Howarth et al.* [1996].
[e] *Pina-Ochoa and Alvarez-Cobelas* [2006].
[f] *Seitzinger* [1988].
[g] See text.

[13] We define Q and direct nonpoint N inputs to each subgrid stream order assuming that runoff and nonpoint N inputs within the grid cell are spatially uniform. Flow path probabilities from stream order *i* to order *j* in the subgrid network are calculated as the proportion of total length in *j* relative to the total length of all stream orders greater than *i*. N removal within each stream order along a flow path is determined using (2) as described by *Wollheim et al.* [2006]. Calculated exports from subgrid river networks drain into STN-30 rivers or lakes, where they are explicitly routed.

[14] The surface area of lakes and large reservoirs in each grid cell is based on the GLWD3 data set of *Lehner and Döll* [2004]. Because the topology of lakes is difficult to establish, we represented all lakes within each cell as a composite lake bearing a single cumulative surface area. Lakes intercept runoff generated within the cell plus all discharge from upstream cells. Large reservoirs are assumed to replace STN-30 river channels [*Vörösmarty et al.*, 2003]. The distributions of large rivers, lakes and reservoirs for North America are shown in Figure 2a.

2.3. Hydrological Conditions

[15] Composite runoff fields that integrate observed discharge (Q) at 663 river gauging sites and Water Balance Model (WBM) predicted runoff [*Fekete et al.*, 2002; *Vörösmarty et al.*, 1998] are used to define mean annual Q at both the sub grid and STN-30 scales. In contrast to *Fekete et al.* [2002], we imposed a requirement of exact correspondence with observed Q at all gauging sites. In ungauged regions (27% of actively discharging landmass), the Q fields rely solely on accumulated WBM-computed runoff. Mean annual channel widths (w) are defined as $w = 8.3Q^{0.52}$. This is based on analysis of U.S. stream gages (David Bjerklie, USGS, personal communication, 2006), is consistent with *Leopold et al.* [1964], and assumed valid globally. The width exponent is similar to the 0.5 global average [*Park*, 1977]. The width constant of 8.3 is between previous estimates of 4 and 16 from the Mississippi [*Arora et al.*, 1999; *Donner et al.*, 2002]. Only w is needed to calculate H_L in rivers (3). For lakes and reservoirs, we derive H_L using Q/A_{sw}.

2.4. Biological Processing Rates

[16] Biological N removal activity is represented using the uptake velocity, υ_f, assuming that first-order benthic processes dominate mean annual N removal. The υ_f parameter is commonly measured in stream spiraling studies [*Ensign and Doyle*, 2006] and has been used to calculate carbon and nutrient removal in rivers and lakes [*Caraco and Cole*, 2004; *Donner et al.*, 2002; *Howarth et al.*, 1996; *Kelly et al.*, 1987]. The parameter υ_f is equivalent to U/C_n where U is the areal process rate (mg m^{-2} a^{-1}) and C_n is nutrient concentration in the water column (mg m^{-3}).

[17] υ_f is applied globally assuming local mean annual water temperature controls variability. We assume a reference uptake velocity (TN-υ_{fref}) = 35 m a^{-1} applies to a reference temperature (T_{ref}) of 20°C. A value of 35 m a^{-1} is typical for denitrification based on measurements in both lake and river systems [*Howarth et al.*, 1996; *Pina-Ochoa and Alvarez-Cobelas*, 2006]. Local grid cell υ_f is then determined assuming a factor of 2 change in υ_f for every 10°C change in temperature (i.e., a Q_{10} approach, where Q_{10} = 2 [*Donner et al.*, 2002; *Seitzinger*, 1988]). The relatively high T_{ref} is based on the assumption that most denitrification measurements have occurred during the growing season of temperate regions. Resulting υ_f's range from 8–70 m a^{-1} between 0 and 30°C. Water temperature is determined for all water bodies in each grid from mean annual air temperature using the model of *Mohseni et al.* [1998].

[18] This approach for applying uptake velocities globally requires several assumptions, including that it is independent of N form, C_n (i.e., U increases linearly with C_n), stream size, and water body type. Although these assumptions are debatable, they are necessitated by a lack of information at the global scale. In addition, the global, terrestrial N model (section 2.5) does not distinguish between N forms entering aquatic systems, so N form specific parameters cannot be applied. We assess possible biases that result from these assumptions by evaluating prediction errors against basin characteristics (see section 2.8).

2.5. N Loading to Aquatic Systems

[19] Predictions from a recent global, spatially distributed terrestrial N cycle model are used to load total N (TN) to the river network [*Bouwman et al.*, 2005; *van Drecht et al.*, 2003]. Point source inputs are based on the distribution of population, GDP, population with sewers, and sewage treatment efficiency. Nonpoint sources are calculated from total N inputs (manure, fertilizers, deposition and biological N_2 fixation), minus N uptake (by agricultural crops and grazing animals). In case of surplus, additional losses occur via denitrification in soils and groundwater. Denitrification is a function of temperature, precipitation, water residence times, and soil characteristics. The model predicts high nonpoint N inputs (>1000 kg km^{-2} a^{-1}) in regions with intensive agriculture, high atmospheric N inputs, and tropical systems. Low-N inputs (<250 kg km^{-2} a^{-1}) occur in cold

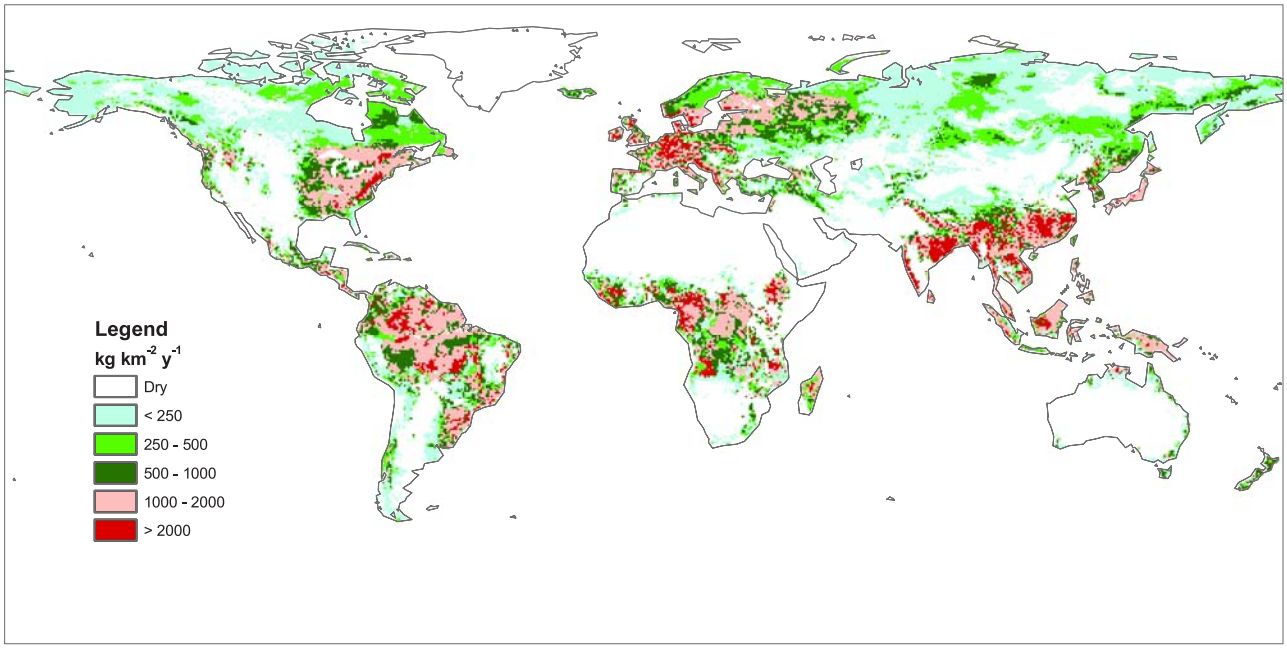

Figure 3. Predicted nonpoint total N (TN) inputs to river systems [*Bouwman et al.*, 2005].

climates and grasslands (Figure 3). Global TN inputs to aquatic systems total 65 Tg N a^{-1} (nonpoint = 59.1; point = 4.7; atmospheric deposition on large lakes = 1.1 Tg N a^{-1}). There are many potential errors in the TN inputs due to the variety of terms and the difficulty validating components (e.g., groundwater denitrification). Further, net retention in natural ecosystems is assumed absent, which may not be correct in some areas (e.g., regrowing forests). For details, see *van Drecht et al.* [2003] and *Bouwman et al.* [2005].

2.6. Observations

[20] We tested TN predictions using observations of contemporary mean annual TN total flux (kg a^{-1}), TN yields (kg km^{-2} a^{-1}), and concentrations (mg N l^{-1}) from 60 globally distributed watersheds compiled in the GEMS-GLORI data set [*Green et al.*, 2004; *Meybeck and Ragu*, 1996]. TN observations in GEMS-GLORI are for the 1986 to 1996 time period, with 50% from between 1993 and 1995 [*Green et al.*, 2004]. This data set has been previously used to calibrate/validate a variety of nutrient models developed for the mid 1990s time frame. TN concentration transects along large river main stems were obtained from the Amazon (CAMREX, 1998, *Amazon River Basin Biogeochemistry, Pre-LBA Data Initiative*, INPE-CPTEC, available at http://lba.cptec.inpe.br/lba/), the Mississippi and Yukon [*Guo et al.*, 2004] (USGS Water Quality Data, available at http://nwis.waterdata.usgs.gov/nwis/), and the Rhine and Danube (EEA River Water Quality Data, 2004, available at http://www.eea.eu.int). We also include mean annual TN concentrations for six major subbasins (Arkansas, Illinois, Upper Mississippi, Missouri, Ohio, Red) within the Mississippi (USGS Water Quality Data).

2.7. Sensitivity Analysis

[21] To understand the factors controlling aquatic TN removal, we explored a number of scenarios that globally varied the hydraulic variables in the model: river drainage density (DD = 2 or 0.06 versus 1.01 in the base scenario), river hydraulic width constants (a = 4 or 14 versus 8.3), river sinuosity (S = 1.1 or 2.0 versus 1.3), lake position within the river network (intercepting local grid cell runoff only), as well as TN-υ_{fref} (υ_{fref} = 60 or 10 versus 35). We also assessed the variation of nonpoint TN inputs (global ±50% compared to the base scenario), and an alternative scenario of TN loading to continental surfaces using *Green et al.* [2004] coupled with the terrestrial transfer efficiencies of *Bouwman et al.* [2005]. In each case, changes in proportional removal by each water body were evaluated, using the Mississippi River basin as the test case.

2.8. Statistics

[22] Relative prediction errors (E, %) for mean annual TN total flux (kg a^{-1}), TN yield (kg km^{-2} a^{-1}), and TN concentration (mg N l^{-1}) at basin mouths were analyzed [*Alexander et al.*, 2002]:

$$E_i = 100\,(P_i - O_i)/O_i \tag{4}$$

where P_i and O_i are the predicted and observed values for each basin i, respectively. We determined bias using the median of the E_i's. Variability of the E_i's was evaluated using the interquartile range (IQR, difference between 25th and 75th percentiles). Exploratory analysis of scatterplots of E_i against various basin factors was used to identify potential sources of error not accounted for by our model [*Alexander et al.*, 2002]. Factors considered included mean

basin runoff, temperature, mean TN concentration entering aquatic system, observed TN concentration at the mouth, and dissolve inorganic to organic N (DIN:DON) ratio observed at the mouth. Slopes and intercepts of observed versus predicted for TN flux, areal flux, and concentrations were estimated using results from the base model. Log transforms were needed to meet assumptions of constant variance and normality. We used a general likelihood ratio test to simultaneously test whether slopes differed from 1 and intercepts from 0 [*Rice*, 2007].

3. Results

3.1. Global River Network Characteristics

[23] Under the assumptions listed in Table 1, at least one fifth-order river network (drainage area = 1066 km^2) occurs in each grid cell, consistent with *Vörösmarty et al.* [2000]. Global length of streams and rivers in flowing regions is 88.2×10^6 km, of which 4.3×10^6 km are large rivers represented explicitly by the STN-30 river network. Grid cells with no runoff and/or discharge are not included in these estimates. Mean global drainage density (total river length/watershed area) for regions with flow is 1.01 km^{-1}. Mean length, mean drainage area, global number, and global length of rivers in each order class are shown in Figure S1.[1]

[24] Global benthic surface area is dominated by lakes (20×10^5 km^2, excluding the Caspian and Aral seas), followed by large rivers (2.95×10^5 km^2), small rivers (2.75×10^5 km^2), and large reservoirs (2.5×10^5 km^2) (Figure 2b). Benthic surface area increases with order within individual basins, in keeping with previous observations [*Naiman*, 1983]. However, as a global total, the distribution of benthic surface area is relatively constant across river orders (Figure 2b).

3.2. Predicted TN Fluxes at Basin Mouths

[25] Predictions at basin mouths show relatively small negative bias, with median prediction errors (E) for TN flux, TN yield and TN concentration of −4.4%, −4.2%, and −11.5%, respectively (Table 2). Variability (based on interquartile range, IQR) ranged between 80% and 90%. Median E's were not significantly different from 0 (Wilcoxon signed rank test, $p > 0.1$ for each). The 25th and 75th percentiles show symmetry around 0, also suggesting little overall bias across basins. The full model has far less bias compared to the no aquatic removal scenario (bias 103–110%, Wilcoxon $p < 0.001$), or globally uniform 30% aquatic removal (bias 42–47%, Wilcoxon $p < 0.001$) derived from *Bouwman et al.* [2005] (Table 2). IQR is also reduced in the full model compared with these other scenarios. Runoff and Q in the model are benchmarked to observations, resulting in Q estimates very similar to those reported in GEMS-GLORI (Table 2).

[26] Although overall bias was small, TN concentration E's showed a relationship with mean basin runoff for basins with runoff <500 mm a^{-1} (Figure 4b). Median E was −36% for basins with runoff <250 mm a^{-1} (n = 30), 54% for basins between 250 and 500 mm a^{-1} (n = 23), and 4% for basins >500 mm a^{-1} (n = 7). Relationships between E and other factors were not found.

Table 2. Prediction Errors Based on n = 60 Basins, Assuming No Aquatic Removal (Conservative Mixing of Terrestrial Inputs; υ_f = 0), Uniform 70% Aquatic Transfer Efficiency as by *Bouwman et al.* [2005] (Uniform), and Using the Full Model (Base Scenario).

Variable/Model	Median	25th Percentile	75th Percentile	IQR[a]
TN flux				
$\upsilon_f = 0$	110.3	34.0	281	247
Uniform	47.2	−6.0	167	173
Full model (base)	−4.4	−36.4	43.7	80
TN areal flux				
$\upsilon_f = 0$	103.0	21.4	252	231
Uniform	42.1	−15.0	146	161
Full model (base)	−4.2	−42.4	48.9	91
TN concentration				
$\upsilon_f = 0$	108.4	26.7	272	245
Uniform	45.7	−11.3	161	172
Full model (base)	−11.5	−42.0	43.0	85
Discharge	2.9	−2.8	17.3	20

[a]IQR: interquartile range. Units for prediction errors are percent. TN is total N.

[27] Direct comparisons of observed and predicted values indicate deviations from the 1:1 line (Figure 5). The general likelihood test, which simultaneously tests for slope = 1 and intercept = 0, indicates significant deviation from the 1:1 line in each case ($p < 0.01$) (Table S2). The relationships were only slightly improved by the removal of the two low extreme outliers in Figures 5b and 5c. Slopes were less than 1 in each case (Table S2), largely driven by modeled values going well below those observed at the low end of the range (Figure 5c). Because discharge and runoff are benchmarked to observations, the deviations for all three measures arise primarily from the predicted concentrations. Use of an alternative global TN input data set [*Green et al.*, 2004] to drive the *Bouwman et al.* [2005] terrestrial model yielded a similar pattern, indicating that the biases are not specific to the data sets used for N inputs onto land.

3.3. Within-Basin Transects

[28] Along five large river main stems, spatial trends in predicted TN concentration generally correspond well with observed trends (Figure 6). The distribution of N inputs to the aquatic system determines potential levels and longitudinal patterns, while aquatic processing shifts the actual trajectory downward to varying degrees. While absolute predicted TN concentrations are reasonable in the Danube and Amazon basins, they are biased high in the Rhine and low in the Mississippi and Yukon. In the Mississippi, the bias is partly due to low predicted TN inputs to the lower Missouri River, as observed concentrations are higher than predicted assuming no aquatic processing (Figure 6c). In the Yukon, TN inputs to aquatic systems appear underpredicted in the lower reaches, while aquatic removal shifts levels further below observations. The direction of error in these transects is consistent with the runoff related bias noted in Figure 4b.

[1]Auxiliary materials are available in the HTML. doi:10.1029/2007GB002963.

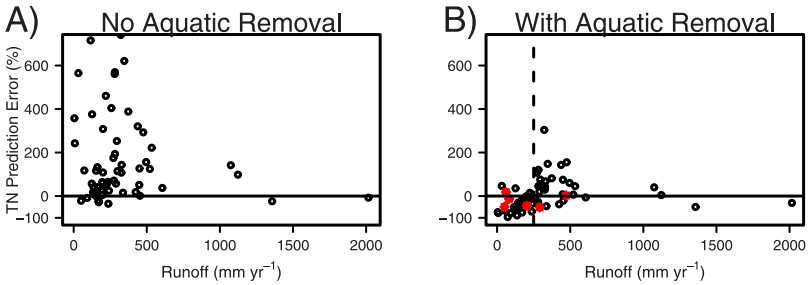

Figure 4. TN concentration prediction errors versus runoff (a) assuming no aquatic removal (i.e., conservative mixing of all inputs to aquatic systems) and (b) after incorporating the aquatic removal model (base scenario, Table 1). Stars in Figure 4b represent the six Mississippi River subbasins.

3.4. Sensitivity Analysis

[29] Removal by the river network was most affected by the biological parameter $\upsilon_{\text{f-ref}}$, followed by the width constant (a) (Table 3). Sinuosity (S) and drainage density (DD) had relatively little impact, while changes in nonpoint inputs did not affect aquatic removal proportions because of the assumption of first-order aquatic process rates. A relatively small range in υ_{fref} (10–60 m a^{-1}) corresponded with an aquatic removal range of 31 to 74% in the Mississippi basin (base removal = 60%). The υ_{fref} = 10 scenario (with mean Mississippi υ_{f} = 5.4 m a^{-1}) corresponded more closely with observed TN concentration in that basin (Table 3). The biological factor in the model has the greatest influence because all aquatic systems are affected, whereas assumptions regarding DD, a, and S directly affect only removal by rivers. Although we focus on sensitivity in the Mississippi basin, similar results were found at the global scale.

[30] Changes in removal by one aquatic subsystem are countered to some extent by the response of other systems, buffering changes in export at the basin mouth. For example, excluding small rivers altogether (DD = 0.06 km^{-1}; Sc2), as would occur if simulating only STN-30 rivers, resulted in the loss of 16.3% small river removal but only a 6.4% export increase because removal by large rivers, lakes and reservoirs increased (Table 3). Similarly, increasing S to 2 (from 1.3 in the base scenario), increased combined river removal to 39% (from 28%), while combined lake and reservoir removal decline to 25% (from 29%) (e.g., Sc8 versus Base, Table 3). A similar response occurs when changing the width constant (e.g., Sc4 versus Base, Table 3).

[31] In the base scenario, lakes were positioned so that H_L is defined by total Q through the grid cell and removal operates on all inputs from upstream grid cells. The scenario that assumes lakes intercept only local runoff (after passage through the subgrid river network) (Sc11) led to small declines in lake removal (~2.5%, Table 3). Use of an alternative data set of N loading to continental surfaces [*Green et al.*, 2004] also resulted in small changes in the Mississippi and globally (Sc12 in Table 3).

[32] Of the factors considered, only nonpoint N inputs and $\upsilon_{\text{f-ref}}$ had sufficiently large influence to impact the runoff related bias in Figure 4b (Table 3). In low-runoff

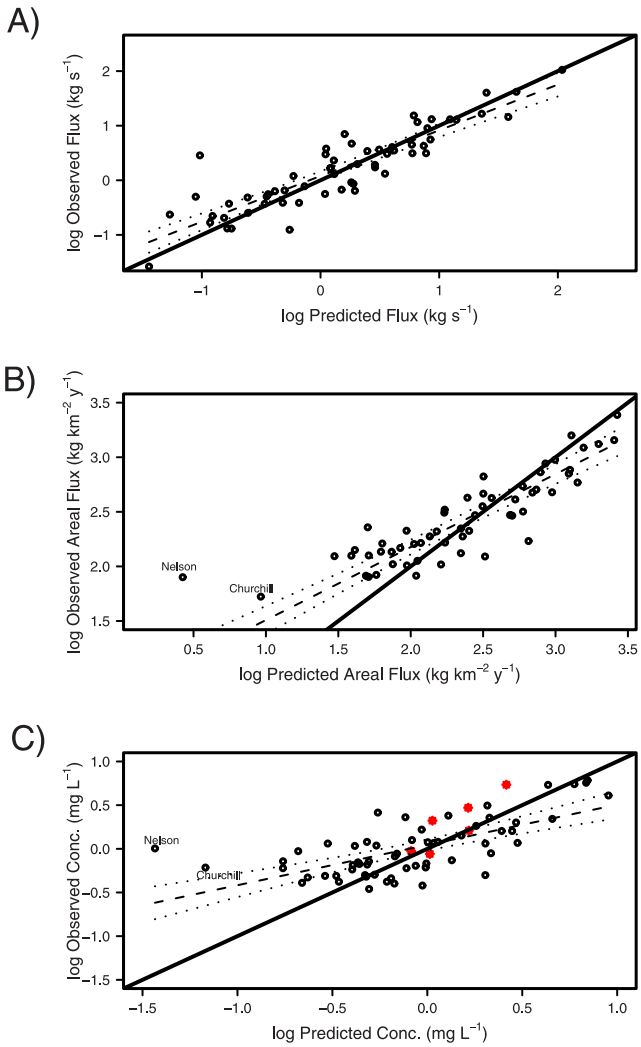

Figure 5. Log observed versus log predicted from the base scenario for (a) TN total flux, (b) TN yield, and (c) TN concentration using the 60 GEMS-GLORI basins with mean annual TN observations. The fitted relationship (dashed line) with 95% confidence interval (dotted lines) are shown. 1:1 line is shown by the solid line. Stars in Figure 5c are for six major Mississippi River subbasins.

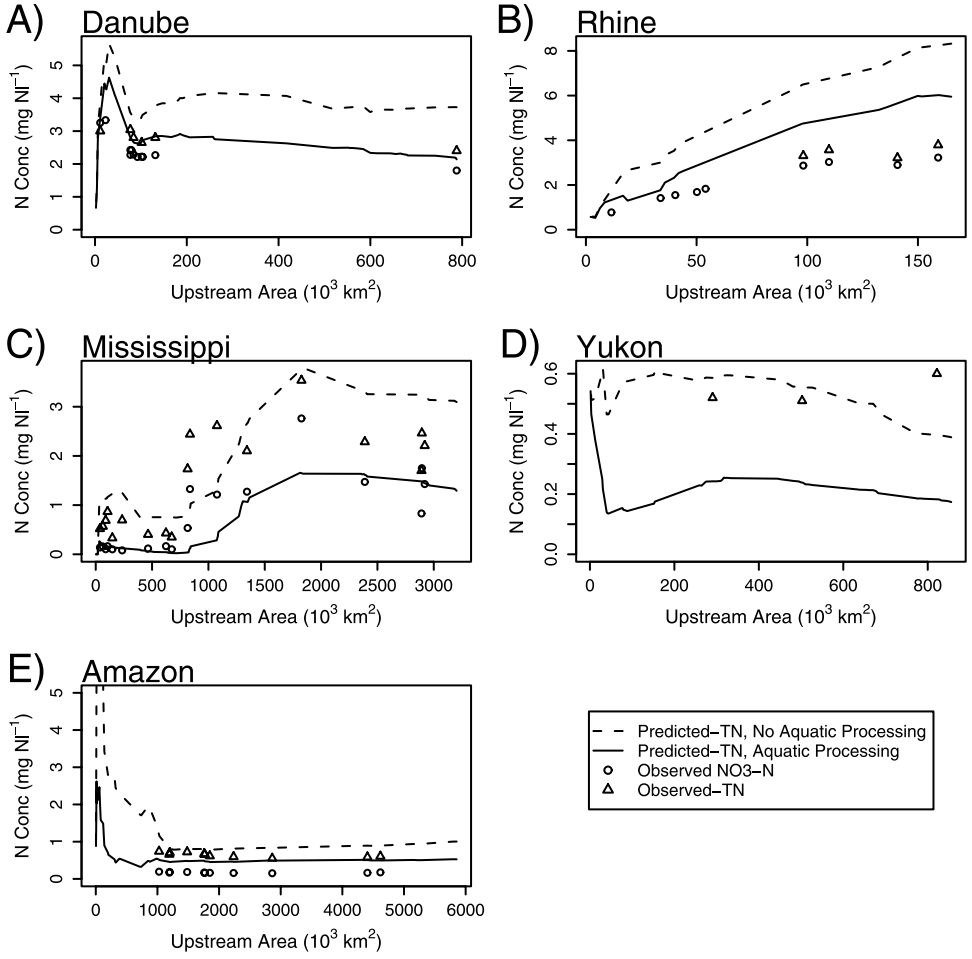

Figure 6. Predicted (base scenario) and observed mean annual TN concentrations along the longest main stem branch in the (a) Danube, (b) Rhine, (c) Mississippi, (d) Yukon, and (e) Amazon. Observed NO_3 transects are also shown for comparison.

Table 3. Results of Sensitivity Analysis[a]

		Drainage Density		Width Constant		$v_{f\text{-}ref}$		Sinuosity		Nonpoint N Input		Local Lake	Green Loads
		2.03	0.06	14	4	60	10	1.1	2.0	+50%	−50%		
Fate of N	Base	Sc1	Sc2	Sc3	Sc4	Sc5	Sc6	Sc7	Sc8	Sc9	Sc10	Sc11	Sc12
Global E, median %													
Basin runoff 0–250	**−36**	−37	−28	−48	−28	−57	**+11**	−34	−48	**−9.1**	−67	−32	−55
Runoff 250–500	**54**	52	68	33	68	**7.5**	114	58	34	130	**−23**	39	26
Runoff > 500	**4**	2	21	−15	27	−30	63	11	−15	54	−42	12	−7
Mississippi E, %	**−46**	−47	−38	−56	−35	−65	−8.6	−43	−56	−22	−71	−44	−53
Miss. Removal, %													
Small River	**16.3**	17.9	0.0	24.2	9.5	24.2	6.3	14.7	22.9	16.7	15.3	16.3	15.4
Large River	**12.1**	11.9	14.8	15.3	7.4	15.1	5.4	10.8	16.3	12.3	12.4	12.6	12.1
Lake	**21.3**	20.8	27.2	18.5	24.0	24.2	12.0	22.0	18.8	21.3	21.5	18.8	21.2
Reservoir	**6.6**	6.4	7.9	5.7	7.4	6.6	4.4	6.8	5.8	6.6	6.5	6.9	6.8
Other	**3.4**	3.4	3.4	3.4	3.4	3.4	3.4	3.3	3.5	3.2	3.7	3.4	3.6
Miss. Export, %	**40.3**	39.6	46.7	32.9	48.4	26.5	68.5	42.4	32.7	40.0	40.6	41.9	40.9
Miss. Export Conc., mg N l^{-1}	**1.29**	1.27	1.50	1.05	1.55	0.85	2.19	1.36	1.05	1.88	0.69	1.34	1.12

[a]Median prediction errors (E) for global basins in different mean runoff categories and for the Mississippi and fate of N entering aquatic system of the Mississippi basin, for different scenarios. The category and value of the parameter changed is noted at the top of each column. TN concentration E's are divided into low (n = 30), moderate (n = 23), and high (n = 7) runoff categories (Figure 4b). Parameter changes relative to Table 1 (base) are for Sc1: A_1 = 0.55 km^2 and L_1 = 0.67 km; Sc2: no subgrid cell rivers; Sc3: a = 14; Sc4: a = 4; Sc5: v_{fref} = 60 m a^{-1}; Sc6: v_{fref} = 10 m a^{-1}; Sc7: S = 1.1; Sc8: S = 2.0; Sc9: nonpoint N inputs increased in each grid cell by 50%; Sc10: nonpoint N inputs decreased in each grid cell by 50%; Sc11: lake removal acts on local grid runoff only; Sc12: *Green et al.* [2004] TN inputs to land coupled with *Bouwman et al.* [2005] terrestrial transfer efficiencies. For the Mississippi, the observed proportion of aquatic inputs exported = 69%, and TN export concentration is 2.4 mg l^{-1}. Bolded entries under Sc5, Sc6, Sc9, and Sc10 indicate the greatest improvement relative to the base scenario.

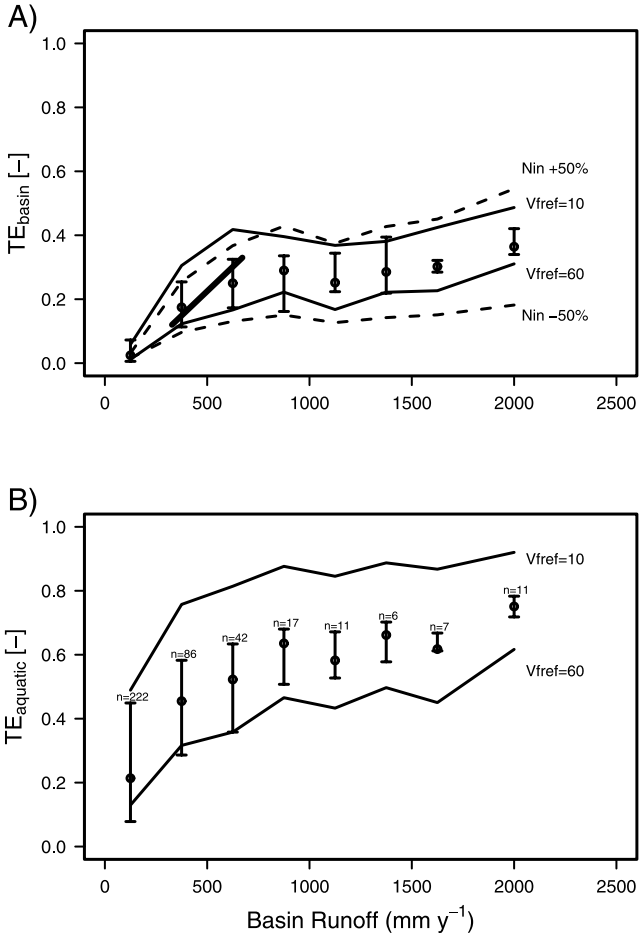

Figure 7. Model-predicted median (a) TE_{basin} versus mean basin runoff and (b) $TE_{aquatic}$ versus runoff for the base scenario (points) and several other scenarios (lines). Basins are binned according to runoff in 250-mm increments (last point includes all basins with runoff >1750 mm a^{-1}). Error bars for the base scenario denote the 25th and 75th percentiles for *n* watersheds in each runoff class (shown in Figure 7b). Lines for selected scenarios (Table 3) show median values. Linear regression reported by *Howarth et al.* [2006] is shown in Figure 7a.

basins (<250 mm a^{-1}), a 50% increase in nonpoint N inputs (Sc9) resulted in median E of −9.1%, compared with −36% in the base scenario. The low-υ_{fref} scenario (Sc6) resulted in median E in low-runoff basins of +11%. A 50% decline in nonpoint inputs (Sc10) or higher-υ_{fref} (Sc5) reduced E in moderate runoff basins (250–500 mm a^{-1}).

3.5. Controls of TN Export

[33] Across all global basins larger than 25,000 km^2 (*n* = 402), the predicted proportion of total basin TN inputs exported (TE_{basin}) increased with basin runoff, from <5–40% (Figure 7a), with a relatively slow increase above 750 mm a^{-1}. No relationship was evident between TE_{basin} and mean basin temperature. The predicted proportion of total aquatic TN inputs exported ($TE_{aquatic}$) also increased with runoff, but with considerably more variability than for TE_{basin} (Figure 7b). $TE_{aquatic}$ showed no pattern against basin temperature, but was constrained to <0.6 when lake proportion was >5% or basin area >1,000,000 km^2 (not shown). Lakes and reservoirs can be an important component of the aquatic N budget when they exceed 1% of basin area (Figure S2). $TE_{aquatic}$ is sensitive to υ_{fref}, but not to changes in N inputs due to the first-order uptake assumption (Figure 7b).

[34] The importance of aquatic relative to terrestrial removal was greatest at intermediate runoffs (Figure S3). In low-runoff regions (<250 mm a^{-1}), aquatic removal was unimportant (<10% of total basin removal). Aquatic removal reached maximum importance (25–35% of total basin removal) in moderate runoff basins (250–750 mm a^{-1}). In these basins, removal by terrestrial systems is reduced, while hydrologic conditions remain relatively favorable for aquatic removal.

3.6. Global Importance of Streams, Rivers, Lakes, and Reservoirs

[35] Global TN removal by aquatic systems predicted by the model is 34.5 Tg a^{-1}, representing 53% of predicted inputs to aquatic systems (65.0 Tg a^{-1}) or 14% of TN loading to continental surfaces (238.7 Tg a^{-1}) (Table 4). Removal by small rivers accounted for 16.5%, large rivers 13.6%, lakes 15.2%, and large reservoirs 5.2% of inputs to aquatic systems. An additional 2.2% was accounted for by large river drying and slight discrepancies between terrestrial model predictions and the global runoff field. The importance of each water body type varied across basins, depending on runoff, temperature, and lake and reservoir abundance (Table S1).

[36] The relative importance of rivers and lakes in the global aquatic N cycle can be explained by the geography of N inputs and benthic surface area. Globally, benthic surface area is dominated by lakes that are concentrated between 40° and 70° N (Figure 8a). In this zone, N removal integrated within latitudinal bands is also dominated by lakes (Figure 8b). However, the considerable aquatic N input that occurs outside this region is dominated by river N removal, especially in the tropics. Large reservoirs are generally of lesser importance.

[37] A composite scenario that applies Sc6 and Sc5 to 0–250 and 250–500 mm a^{-1} basins, respectively, to account for bias related to runoff minimally affected both the global

Table 4. Modeled Fate of Global TN Inputs to Aquatic Systems

Compartment	Base Scenario
Total inputs to basins, Tg N a^{-1}	238.7
Inputs to aquatic, Tg N a^{-1}	65.0
Removal	
Small (subgrid) rivers, %	16.5
Large rivers, %	13.6
Lakes, small reservoirs, %	15.2
Large reservoirs, %	5.2
Other, %	2.2
Total aquatic removal, %	52.7
Export, %	47.3

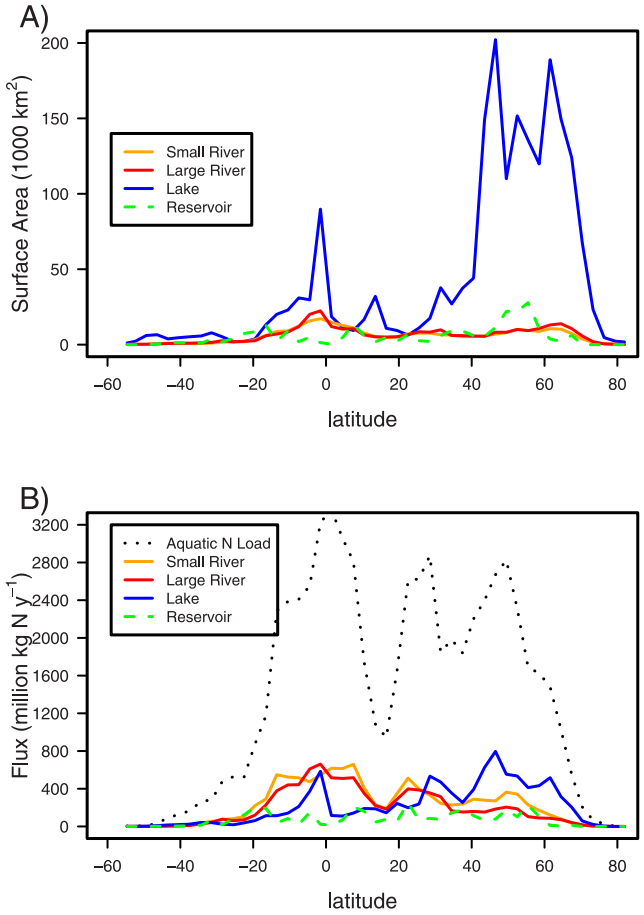

Figure 8. Global distribution as a function of latitude for (a) benthic surface area (km^2) of small rivers, large rivers, lakes, and reservoirs and (b) N Loading to aquatic systems and N removal by each water body type. Values are binned over 3° latitudinal bands.

aquatic removal proportions and the distribution of removal by latitude. Basins in both runoff categories account for a similar proportion of global N inputs to aquatic systems (∼25% to each).

4. Discussion

4.1. Within-Basin Aquatic N Modeling at the Global Scale

[38] A within-basin, spatially distributed approach is necessary to understand the fate of N within aquatic systems globally. This necessity arises because connectivity over long distances via rivers is an integral feature of aquatic systems, requiring knowledge of source distributions and the accumulated processes along surface water flow paths [*Alexander et al.*, 2000]. The role of a given water body within a river network will be highly dependent on its position, and the amount of material reaching it. For example, the importance of lakes in the global N cycle is less than might be expected on the basis of their surface area (Figure 8), because they do not intercept large amounts of N entering global river systems. Thus, assessing how global nutrient fluxes are altered by multiple anthropogenic changes (sources, distributions, hydrology, biology) requires a spatially explicit perspective.

[39] Both the terrestrial and aquatic models applied here were structured and parameterized a priori on the basis of available information. The coupled model, therefore, represents a synthesis of the spatially distributed mechanisms controlling mean annual N fluxes at the global scale, including N inputs to land and the key controls of terrestrial and aquatic removal. Overall results compare favorably with calibrated whole basin models developed at the global scale. Median E from a variety of calibrated whole basin models ranged from −23 to 34%, and IQR ranged from 109 to 214% [*Dumont et al.*, 2005]. Despite being uncalibrated, our model shows similar median E and lower IQR (Table 2). However, the underlying runoff related bias suggests that elements of the coupled terrestrial-aquatic model require improvement (see section 4.5).

[40] Aquatic systems exert an important control of N flux to the coastal zone. Although terrestrial systems dominate N removal globally (Figure S3), spatially distributed aquatic models, as a component of whole basin models, will improve predictions of nutrient flux to coastal zones. The addition of the aquatic model reduced overall bias and increased precision compared to *Bouwman et al.* [2005], who assumed a globally uniform 30% aquatic removal rate (Table 2). In our base model, aquatic removal accounted for 50% of global aquatic TN inputs, resulting in lower global TN export (31.4 Tg a^{-1}) than predicted by *Bouwman et al.* [2005]. Our prediction of aquatic removal is at the low end of that reported by *Seitzinger et al.* [2006], who used a statistical approach to estimate aquatic N removal from the same N input data.

[41] Basin-scale aquatic N removal that emerges from the aggregation of local-scale removal in our model is consistent with findings from whole basin models indicating runoff is a primary control of TE [*Caraco and Cole*, 1999; *Howarth et al.*, 2006; *Smith et al.*, 2005]. Other factors such as basin size, temperature, and lake abundance apparently define variability within runoff classes (Figure 7b). Our model thus appears to capture key mechanisms controlling N transfers that can help understand how changes on land (N loading distribution, runoff) and in river systems (e.g., channelization, reservoir construction) will impact global nutrient fluxes.

[42] A spatially distributed within-basin perspective will be needed for globally consistent policy assessments regarding surface water quality and the role of aquatic systems in its maintenance. For N, our results demonstrate the extent to which inputs from land lead to TN concentration exceeding 10 mg N l^{-1} (a threshold of water quality), and the potential for aquatic processes to attenuate these levels. In the base model, aquatic N removal reduced river length exceeding 10 mg N l^{-1} by 46% from 262,000 km (assuming conservative mixing of inputs) to 140,000 km. A composite scenario that accounts for runoff bias (replacing Sc6 in basins with runoff 0–250 mm a^{-1} and Sc5 in basins with 250–500 mm a^{-1}) resulted in 178,000 km of impacted length (a 33% reduction). These results suggest that aquatic

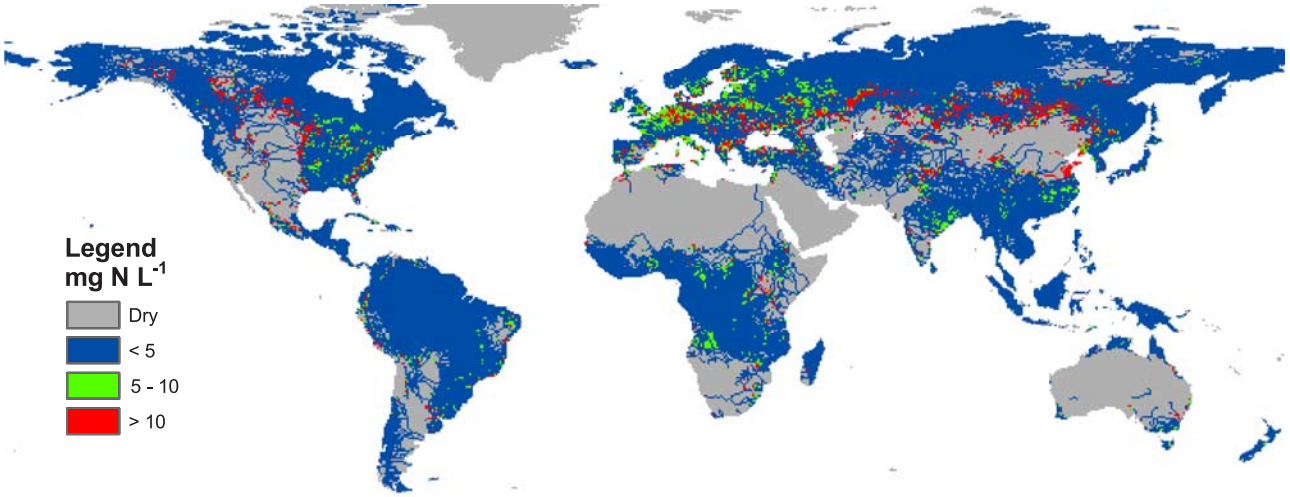

Figure 9. Map of predicted mean annual TN concentration in STN-30 rivers after accounting for terrestrial and aquatic removal processes using the base scenario.

processes play a role in maintaining water quality, but their overall capacity to do so may be limited. In our model, regions of potentially impaired water quality were associated with low-runoff areas with moderately elevated N inputs (e.g., central Asia), and higher-runoff regions with heavy N loading (e.g., Europe, parts of North America) (Figure 9). We note, however, that fine-scale analysis should be conducted with caution, since we tested the model mainly at large basin scales. In addition, the runoff related bias suggests the distribution of high-N concentrations is underestimated in drier regions, and over estimated in wetter regions. Improved observational data sets are needed at the global scale to better test these predictions.

4.2. Biological Controls of Aquatic N Removal

[43] The nitrogen cycle is complex, with numerous transformations among N forms that vary over time and space. In our model, we applied a single removal parameter to TN without consideration of dominant N form (DIN versus DON) across different world basins. This limitation was necessary because of the information available from the terrestrial model. Further, we assumed removal processes were dominated by first-order kinetics. Inadequacies due to these assumptions were not apparent at the global scale, because we found no prediction bias at basin mouths related to aquatic input concentrations, observed export concentrations or DIN:DON export ratios. At the global, mean annual scale, errors that might arise from these assumptions are possibly outweighed by other factors, such as runoff conditions, lake/reservoir abundance, and the position of N inputs relative to these.

[44] However, some of the discrepancies in our model results seem likely because of these simplifying assumptions. For example, the low-TN prediction in the Yukon (Figure 6d), Nelson and Churchill Rivers (Figures 5b and 5c), pan-Arctic rivers where DON dominates annual N fluxes [*Guo et al.*, 2004; *Meybeck and Ragu*, 1996], suggests there is a less reactive N pool that limits N removal. Deficiencies due to the assumption of first-order kinetics are more likely to explain deviations in high-TN basins where DIN dominates. Although many field measurements of denitrification [*Pina-Ochoa and Alvarez-Cobelas*, 2006] and whole basin N budgets [*Howarth et al.*, 1996, *Boyer et al.*, 2002] suggest that N removal is independent of concentration, others have found declining denitrification-υ_f with increasing concentration in streams [*Garcia-Ruiz et al.*, 1998; *O'Brien et al.*, 2007]. The underprediction of TN from high observed N subbasins of the Mississippi (Illinois, Upper Mississippi and Missouri, Figure 5c) suggests that concentration-dependent kinetics might at least be regionally important, but other high-N basins do not show this behavior. The runoff related bias suggests that the relationship between dominant N form, controls of aquatic biological activity, and runoff characteristics should be further explored (see section 4.5).

[45] Of the many N processes, only denitrification and long-term storage influence mean annual N removal. Various syntheses of empirical measurements have suggested that denitrification-υ_f is fairly low (ranging from 0 to 100 m a^{-1}) and constrained relative to assimilatory uptake processes (often much greater than 100 m a^{-1}) [*Howarth et al.*, 1996; *Peterson et al.*, 2001; *Pina-Ochoa and Alvarez-Cobelas*, 2006]. Nevertheless, global implementation of relatively low denitrification-υ_f results in significant aquatic removal consistent with observed exports, aquatic hydrological characteristics, and aquatic TN inputs.

[46] The uptake velocity parameter can be used to scale point measurements to entire networks on the assumption that each unit of benthic surface area has similar first-order areal uptake. Although uptake velocities are likely to vary with a variety of physical, chemical, or biological factors, this assumption allows an independent assessment of biological and surface water hydrological factors leading to N removal [*Wollheim et al.*, 2006]. The assumption is reasonable if variability in surface hydrology across diverse aquatic systems is greater than variability of biological

activity. This assumption should be tested as more information regarding the controls of N removal processes and their spatial distribution becomes available.

[47] The fate of N could be gaseous loss via denitrification or long-term storage in lakes and reservoirs. We do not distinguish between these fates using the single biological rate parameter. *Cole et al.* [2007] recently estimated that carbon storage in lakes and reservoirs was 50 and 180 Tg C a^{-1}, respectively. Assuming 10:1 C:N molar ratio of preserved O.M. in lakes and 20:1 in reservoirs [*Dean and Gorham*, 1998], this would result in 16.3 Tg N a^{-1} sequestered, on the order of the 13 Tg N a^{-1} removed globally by lakes and reservoirs in our model (Table 4). A partitioning of TN removal to denitrification versus storage in global models is needed, and will require coupling C and N dynamics within a river network context.

4.3. Location of Aquatic N Removal

[48] Accounting for smaller rivers (draining basins <1000 km^2) in global analyses will be needed to identify the location of aquatic removal in the landscape. Our model suggests small river networks are disproportionately important in the global aquatic N budget (31% of aquatic removal) compared to their surface area (10% of aquatic surface area) (Table 4). Their importance arises because they first intercept nonpoint inputs that dominate N loading globally [*Meybeck and Vörösmarty*, 2005; *van Drecht et al.*, 2003], and because their surface-to-volume ratios favor removal [*Peterson et al.*, 2001]. The relative importance of small rivers depends on the assumption that uptake velocities are similar across water bodies. No obvious differences in N uptake velocities have been noted across river size [*Ensign and Doyle*, 2006] or between lakes and rivers [*Pina-Ochoa and Alvarez-Cobelas*, 2006], but this requires further evaluation.

[49] Although lakes are clearly important in the global aquatic N cycle [*Seitzinger et al.*, 2006] (Table 4), their role is less than the combined removal by rivers because lakes are concentrated in certain areas and do not intercept much of the global N input to aquatic systems (Figure 8). Extremely small lakes and reservoirs are not considered in our analysis but may contribute considerable additional surface area [*Downing et al.*, 2006; *Vörösmarty et al.*, 2003] that would enhance the role of lakes. In our model, lakes either intercepted all upstream discharge or local runoff only (base scenario and Sc11, Table 3), but these showed only minor differences, possibly because most STN-30 grid cells are first-order segments with no upstream inputs [*Vörösmarty et al.*, 2000]. In reality, most lakes are interspersed throughout the subgrid river network. How this would affect integrated lake N removal would depend on the number, size and "order" of lakes, and prior N removal by upstream systems. The composite role of lakes in a river network context should be explored at finer resolutions. Large reservoirs are relatively unimportant globally, but can be significant in individual basins (Figure S2). Their role is not major because upstream removal limits the amount of N they receive, and because they are not abundant in regions with intensive N inputs (Figure 8).

4.4. Buffering Capacity of River Networks

[50] Downstream aquatic systems can partially buffer changes in the N removal capacity of upstream systems, limiting change in exports. When sinuosity, width, or drainage density is reduced, each lessening removal by rivers, the role of lakes and reservoirs increases because they receive greater inputs. Changes in υ_{fref}, despite being applied to all water bodies, have greater impact on the role of small rivers for this reason as well (Table 3). A similar buffering effect by river networks was previously noted, as declines in υ_f above certain levels did not influence basin exports due to compensatory N removal by larger rivers [*Wollheim et al.*, 2006]. *Seitzinger et al.* [2002] found relatively small proportional change in N export using a high- versus low-resolution river network, despite much longer total river length in the former. The relative effectiveness of small rivers, combined with a buffering effect, can help explain the lack of strong basin area influence in whole basin regression models [*Smith et al.*, 2005]. The existence of a buffering capacity has clear implications for watershed response to anthropogenic N increases and suggests the importance of the within-basin topological approach applied here.

4.5. Uncertainties

[51] Understanding N fluxes in river systems is problematic because of the difficulty separating terrestrial and aquatic signals [*Bernhardt et al.*, 2005]. Only coupled terrestrial-aquatic models can be tested using riverine flux observations. Although TN export predictions using FrAMES are an improvement over assuming uniform aquatic removal, the runoff related bias (Figure 4) suggests improvements in model components (nonpoint inputs, aquatic removal) are needed. Errors associated with estimating observed mean annual TN can also be a factor, and are potentially related to flow regime [*Syvitski et al.*, 2003].

[52] Nonpoint inputs to aquatic systems are defined by total N inputs onto and removal processes within terrestrial systems. Both components have considerable uncertainty. Much of the bias in low-runoff basins (<250 mm a^{-1}) can be explained by increasing nonpoint N inputs 50% (Sc9, Table 3), requiring only a small change in terrestrial TE (median from 0.11 to 0.15). Similarly, <50% reduction in nonpoint inputs can explain the bias in moderate runoff basins, requiring terrestrial TE to decline from 0.39 to 0.21 (Sc 10, Table 3). These are relatively small changes, consistent with less denitrification in drier regions where soils may be less anoxic, or more denitrification in moderate runoff basins where soils cycle between dry and wet conditions (favorable for denitrification). Total N loading may also be biased, but two different N loading data sets (Base, Sc11) resulted in similar outcomes (Table 3), despite having different amounts and distributions of net inputs onto land [*van Drecht et al.*, 2005]. Although bias in the terrestrial model is a possibility, the strong runoff related bias only becomes evident after aquatic removal (Figure 4), suggesting the aquatic model is at least partially responsible.

[53] Runoff-related bias in aquatic removal could arise from both hydrological and biological factors. Drainage density (DD) is often greater at lower runoffs [*Gregory*,

1976], but this should lead to more removal in our model, worsening the bias. Moreover, model results were relatively insensitive to DD (Table 3). Error in sinuosity (S) cannot explain removal estimates that are too high, as reduction toward S = 1 leads to small changes insufficient to explain discrepancies (Table 3). Increased S leads to greater removal, but the changes are also relatively small, in part because of compensatory changes in removal by lakes and reservoirs that are unaffected by S.

[54] The width constant (a) appears to have a greater influence than DD or S (Table 3). The relationship between a and runoff conditions is not known. In contrast to the width exponent, which is relatively constrained on the basis of synthesis of a number of studies [*Park*, 1977], a can vary several-fold even for well-studied basins [e.g., *Arora et al.*, 1999; *Donner et al.*, 2002]. The width constant has the potential to influence basin exports (Table 3), especially in combination with biological variability, so a better understanding of its control is needed.

[55] The bias might result because the aquatic model applied here is based on mean annual conditions. We do not account for most material fluxes occurring during high flows when channel removal capacity declines because of hydraulic changes [*Doyle*, 2005], which may be particularly important in low-runoff systems with flashier hydrology. The effective uptake velocities at mean annual scales could differ depending on the timing of inputs. Predicted aquatic N removal in the Mississippi in our model (~60%) is much higher than the 24% predicted using a daily time step model [*Donner et al.*, 2004]. Comparisons across these models are, however, difficult because of different v_f's, network resolutions, lake abundance and hydraulic relationships. The better fit of the low-v_f scenario in the Mississippi (Sc6, Table 3) is consistent with reduced removal during high flux periods that occur during colder periods when biological activity is reduced. Our model also does not account for periodic linkages with organic matter rich floodplains that have high-N removal capacity [*Johnston et al.*, 2001], possibly explaining high predictions in wetter basins.

5. Conclusions

[56] Understanding the fates of nutrients within basins will require mechanistic models that incorporate spatial and temporal variability of key hydrological, biological and geomorphic factors. Our analysis suggests that aquatic systems play a significant role in the contemporary global N cycle. Relatively low rates of aquatic biological activity lead to significant N removal given the distribution of N inputs, hydrological conditions, and river network geomorphology. Small rivers, large rivers, and lakes contribute similarly, but the global impact of lakes is limited by their distribution relative to N inputs. Runoff is a primary control of aquatic removal capacity, suggesting that an altered hydrologic cycle will have important consequences. However, runoff related bias in our model indicates that improved representation of nonpoint inputs and/or aquatic removal will be needed before fully evaluating the impact. Our focus on mean annual conditions is a first global attempt at spatially explicit modeling of the aquatic N cycle, and is useful for exploring the geography of N removal. Future efforts will extend this analysis to account for time varying hydrological conditions, and to incorporate FrAMES as a component within emerging earth systems models (e.g., GFDL, CSDMS). Spatially distributed models, in conjunction with remote sensing products that provide additional validation targets, will allow consistent assessment of water quality at the global scale (Figure 9), and improved tests of coupled terrestrial-aquatic models. The model presented here is a step toward a fuller understanding of the global role of aquatic systems in the face anthropogenic change.

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